REMARKS

The Applicants' below-named representative would like to thank Examiner Vera Afremova for the helpful and courteous discussion of the issues in this application held on August 10, 2006. This discussion addressed several points raised in the outstanding Office Action. The points addressed during the discussion are identified below.

The outstanding Office Action includes an objection to the characterization of the surfactant in independent claims 1 and 21 as an anionic surfactant. The dependent claims are amended to clearly identify specific anionic surfactants as example of anionic surfactants. Furthermore, it is submitted that the definition of anionic surfactant is well known in the art and the types of surfactant that are considered anionic surfactants are well known in the art. The Examiner's attention is directed to Rosen, Surfactants and Interfacial Phenomena, ©1978 by John Wiley & Sons, Inc., pages 1-25, where the definitions of surfactant and anionic surfactant are provided. In particular, page 1 of Rosen defines a surfactant as "a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces)." Furthermore, according to Rosen on page 4, an anionic surfactants is a surfactant where "the surface-active portion of the molecule bears a negative charge." In view of the amendment to claims 1 and 21 and the enclosed publication by Rosen, it is submitted that one having ordinary skill in the art understands what is meant by a surfactant, and in particular, what is meant by an anionic surfactant.

The outstanding Office Action contents that the meaning of the term "anionic surfactant" is indefinite and therefore cannot be relied upon to distinguish from European Publication No. 0 685 556 to *Ghazarian et al.* This is clearly incorrect. The definition of an anionic surfactant is well known and understood in the art.

The outstanding Office Action contents that "TRIS" is a surfactant in view of page 1664 of the MERCK Index 1996, 12th Edition. It is pointed out that page 1664 of the MERCK Index clearly identifies TRIS as a buffer. In the paragraph entitled "Use," the MERCK Index provides that TRIS can be used in the synthesis of various components including surface-active agents. Furthermore, this paragraph provides that TRIS can be used in various compositions where a buffer is normally found. It is incorrect to characterize TRIS as a surfactant on the grounds that it can be used in the preparation of a surfactant or in a composition that contains a surfactant

(e.g., an emulsion). Furthermore, the structure for TRIS provided by the MERCK Index is not consistent with the definition of surfactant provided by Rosen. The outstanding Office Action fails to provide any explanation of why the structure of TRIS would be a component that adsorbs onto the surfaces or interfaces of a system to alter to a marked degree the surface or interfacial free energies of those surfaces or interfaces. Clearly, TRIS is not a surfactant but rather is a well known buffer.

The outstanding Office Action argues that component (b) "is not necessarily one specific ingredient as argued." It is pointed out that claims 1 and 21 clearly identify the presence of an anionic surfactant. Furthermore, the definition of an anionic surfactant is well known in the art. The contention in the outstanding Office Action that "glycerol, fructose, glucose, etc." are examples of anionic surfactants is clearly incorrect. The outstanding Office Action has not established that glycerol, fructose, or glucose are surfactants, and clearly has not established that these components are anionic surfactants.

The outstanding Office Action contents that the BILADYL concentrate contains egg yolk. It is pointed out the BILADYL concentrate does not contain egg yolk. Exhibit B of Dr. Richard Lomneth's Declaration (mailed on March 31, 2005) includes recipes for the use of the BILADYL concentrate. The company distributing the BILADYL product, Minitüb GmbH, teaches the addition of egg yolk to the BILADYL concentrate. However, the BILADYL concentrate itself does not include egg yolk. The Examiner's attention is directed to the copy of the label of BILADYL concentrate enclosed with this Amendment. The label of BILADYL concentrate does not identify egg yolk as an ingredient. The interpretation in the outstanding Office Action that the BILADYL concentrate contains egg yolk is clearly incorrect.

It is understood that the Declaration by Dr. Richard Lomneth was essentially ignored in view of the incorrect contention that the BILADYL concentrate contains egg yolk. Because the BILADYL concentrate does not contain egg yolk, it is submitted that this rationale for ignoring the Declaration by Dr. Richard Lomneth is without merit, and reconsideration of the Declaration of Dr. Richard Lomneth is requested.

The remaining comments provided in the outstanding Office Action, and as discussed during the interview with Examiner Vera Afremova, are summarized and explained upon in the following remarks.

Rejection Under 35 U.S.C. § 112

The outstanding Office Action includes a rejection of claims 1, 2, 4-6, 9-11, 13, 14, 21, 22, 24-26, 28-31, 33, and 34 under 35 U.S.C. § 112, second paragraph. This rejection is traversed.

The basis for this rejection relates to confusion over the definition of an anionic surfactant. Enclosed for the Examiner's reference is a copy of Chapter 1 of Rosen, Surfactants and Interfacial Phenomena, ©1978 John Wiley & Sons, Inc., pages 1-25. On page 1 of Rosen, a surface active agent (surfactant) is defined as "a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces)." Furthermore, according to Rosen on page 4, anionic surfactants are those components where "the surface-active portion of the molecule bears a negative charge." Clearly, the art understands what is meant by the phrase "anionic surfactant."

Claims 9 and 33 are amended to more clearly provide that the list of surfactants are anionic surfactants. Furthermore, the amendment cancels claims 10 and 34.

In view of the above explanation and the amendment to the claims, withdrawal of this rejection is requested.

Prior Art-Based Rejections

The present invention is directed to an aqueous ready to use semen extender composition. The semen extender composition includes about 0.1 wt.% to about 6 wt.% phospholipid obtained from non-animal source comprising lecithin, about 0.0001 wt.% to about 1 wt.% of anionic surfactant to reduce ice crystal formation during freezing of the composition, about 0.5 wt.% to about 3 wt.% carbohydrate, about 3 wt.% to about 14 wt.% freeze agent, and biological buffer to provide the composition with a pH of about 6.9 to about 7.5, and a sufficient amount of water so that the composition exhibits an osmolality of about 250 mOsM to about 350 mOsM, and wherein the composition is substantially free of animal products. The claimed invention is additionally directed to a method for manufacturing an aqueous ready to use semen extender composition.

One advantage of the aqueous ready to use semen extender composition according to the present invention is the ability to avoid the use of egg yolk which is a common component in

conventional semen extender compositions while providing a semen extender composition that provides a desired level of viability and motility of the sperm cells. It is believed that egg yolk may contain nonpathogenic organisms or pathogenic organisms that may be harmful to the host or cells that contact the product. Accordingly, eliminating egg yolk from the ready to use semen extender composition reduces the risk of contamination of the semen by organisms that may be present in the egg yolk.

Rejection Over European Publication No. 0 685 556 (*Ghazarian et al.*)

Claims 1, 2, 6, 8, 11, 13, 14, 21, and 22 stand rejected under 35 U.S.C. §102(b) over *Ghazarian et al.* This rejection is traversed.

Ghazarian et al. fail to disclose an aqueous ready to use semen extender composition containing about 0.0001 wt.% to about 1 wt.% of an anionic surfactant to reduce ice crystal formation during the freezing of the composition according to the present invention.

Because *Ghazarian et al.* fail to disclose an aqueous ready to use semen extender composition containing about 0.0001 wt.% to about 1 wt.% of anionic surfactant to reduce ice crystal formation during freezing of the composition according to the present invention, the claimed invention is not anticipated by *Ghazarian et al.* and withdrawal of this rejection is requested.

Rejection Over U.S. Patent No. 6,368,786 (*Saint-Ramon et al.*)

Claims 1, 2, 4-6, 8, 11, 13, 14, 21, and 22 stand rejected under 35 U.S.C. §102(e) over *Saint-Ramon et al.* This rejection is traversed.

Along with the amendment mailed on March 29, 2005, a Declaration by Dr. Richard Lomneth was provided to demonstrate a reduction to practice of the invention prior to May 14, 1999 corresponding to the priority date of *Saint-Ramon et al.* According to the outstanding Office Action at page 9, the Declaration was disregarded on the grounds that the BILADYL product does contain egg yolk, and therefore the product referred to in the declaration contains egg yolk. As discussed above, the BILADYL concentrate does not contain egg yolk. The Examiner's attention is directed at the product label enclosed with this amendment. The product label for the BILADYL concentrate does not identify egg yolk as a component. BILADYL concentrate is a commercially available product that is intended to be used with egg yolk. The

Examiner's attention is directed at Exhibit B provided as part of the Declaration by Dr. Richard Lomneth. Exhibit B includes instructions for preparing a "cocktail AB." In particular, according to the instructions, "100 ml clean egg yolk from fresh chicken eggs" is added during the preparation of solution A and during the preparation of solution B. The BILADYL concentrate itself does not contain egg yolk. The BILADYL concentrate referred to in the Declaration by Dr. Richard Lomneth does not contain egg yolk.

The Examiner is requested to reconsider the Declaration by Dr. Richard Lomneth in view of the incorrect interpretation of the Declaration expressed in the outstanding Office Action.

The Declaration by Dr. Richard Lomneth clearly demonstrates possession of the invention of the above-identified patent application as a result of a reduction to practice of the invention prior to May 14, 1999. In view of the Declaration by Dr. Richard Lomneth, *Saint-Ramon et al.* does not qualify as prior art under 35 U.S.C. §102(e), and withdrawal of the rejection over *Saint-Ramon et al.* is requested.

Rejection over *Ghazarian et al.* or *Saint-Ramon et al.* in view of U.S. Patent No. 3,444,039 (*Rajamannan*), U.S. Patent No. 6,130,034 (*Aitken*), U.S. Patent No. 6,140,121 (*Ellington et al.*), C. Helleman and E. Gieroux, Deep Freezing of Rabbit Sperm, Effect of a Surfactant on Fertilizing Capacity, Zuchthyg., 23, 33-37 (1988) (*Hellemann et al.*)

Claims 1, 2, 4-6, 8-11, 13, 14, 21, 22, 24-26, and 28-31 stand rejected under 35 U.S.C. §103(a) over *Ghazarian et al.* or *Saint-Ramon et al.* and *Rajamannan*, *Aitken*, *Ellington et al.*, and *Helleman et al.* This rejection is traversed.

In view of the above comments, *Saint-Ramon et al.* are not available as prior art. Accordingly, withdrawal of this rejection as it is based upon *Saint-Ramon et al.* is requested.

As discussed previously, *Ghazarian et al.* fail to disclose an aqueous ready to use semen extender composition comprising about 0.0001 wt.% to about 1 wt.% of anionic surfactant to reduce ice crystal formation during freezing of the composition according to the present invention. It is submitted that the references relied upon in the outstanding Office Action would not have suggested modifying *Ghazarian et al.* to include an anionic surfactant.

Ghazarian et al. are directed to a vehicle for nonautonomous microorganisms of the animal kingdom to be kept alive outside their natural environment with a view to human interventions. The vehicle includes an aqueous medium comprising nutrition agents, buffers and

mineral salts, and a protective product formed as a support for embryonic growth by a living organism, wherein the protective product is a lecithin extracted from soy seeds and introduced into the aqueous medium upon formation of the vehicle. See the English language translation of *Ghazarian et al.* on page 2, lines 1-17, and page 3, lines 20-27.

As discussed above, *Ghazarian et al.* fail to disclose a composition containing about 0.0001 wt.% to about 1 wt.% of anionic surfactant to reduce ice crystal formation during freezing of the composition. *Rajamannan*, *Aitken*, *Ellington et al.*, and *Hellemann et al.* would not have suggested modifying *Ghazarian et al.* to include about 0.0001 wt.% to about 1 wt.% of anionic surfactant to reduce ice crystal formation during freezing of the composition according to the presently claimed invention.

Rajamannan appears to be relied upon in the outstanding Office Action for the disclosure of buffering to a pH of 6 to 7.5 and for the disclosure of sodium citrate as a buffering agent. See *Rajamannan* at column 3, line 30 and lines 41-47. It is pointed out that *Rajamannan* is directed at an egg yolk containing composition. See *Rajamannan* at column 1, lines 13-19, and the example disclosing the presence of egg yolk solids. It is pointed out that *Rajamannan* fails to disclose or suggest the use of about 0.0001 wt.% to about 1 wt.% anionic surfactant to reduce ice crystal formation during freezing of the composition according to the present invention.

It appears that the outstanding Office Action relies upon *Aitken* for the disclosure of an anti-oxidant. *Aitken* refers to an anti-oxidant such as vitamin E at column 1, line 50. It is pointed out, however, that Aitken is directed at an egg yolk-containing system. See *Aitken* at column 1, lines 28-38. The outstanding Office Action fails to explain why one having ordinary skill in the art would look to a disclosure relating to the use of raw egg yolk for a suggestion to modify a composition that is free of raw egg yolk.

It is submitted that raw egg yolk contains a large number of various components and is a much more complicated system than the semen extender composition that does not contain raw egg yolk. Accordingly, the disclosure of the use of an anti-oxidant in a raw egg containing semen extender composition according to *Aitken* in no way suggests the use of an anti-oxidant in a non-raw egg containing semen extender composition.

Nevertheless, the outstanding Office Action fails to explain why one having ordinary skill in the art would receive a suggestion from *Aitken* to modify *Ghazarian et al.* to include

about 0.0001 wt.% to about 1 wt.% anionic surfactant to reduce ice crystal formation during freezing of the composition according to the present invention.

The outstanding Office Action appears to rely on *Ellington et al.* for the disclosure of various buffers such as EDTA and TRIS. See *Ellington et al.* at column 16, lines 52-63, and column 19, line 28. The outstanding Office Action additionally refers to *Ellington et al.* for the disclosure of a balanced culture medium such as M199 at column 16, line 59, and contends that medium M199 suggests the use of polyoxyethylene sorbitan (Tween 80). It is submitted that Tween 80 is provided in medium M199 to help dissolve the other components in medium M199. There is no disclosure by *Ellington et al.* or ATCC Catalogue (Page 522) that Tween 80 can be useful for reducing ice crystal formation during freezing of a semen extender composition. One having ordinary skill in the art would not have received any suggestion from *Ellington et al.* or ATCC Catalogue (Page 522) that the incorporation of Tween 80 into the composition described by *Ghazarian et al.* would have any benefit for reducing ice crystal formation during freezing according to the present invention. Accordingly, no reason has been provided to explain why one having ordinary skill in the art would be motivated to modify *Ghazarian et al.* to include Tween 80 which is simply a disclosed component of medium M199.

The reliance upon *Ellington et al.* and ATCC Catalogue (Page 522) is an example of the use of impermissible hindsight. There must be a suggestion to combine the references or make the modifications to achieve a *prima facie* case of obviousness. It is not enough to simply pick and choose various components from several references. The outstanding Office Action fails to explain why one having ordinary skill in the art would be motivated to select Tween 80 from the lengthy list of components identified in balanced culture M199, and then add that component to the composition described by *Ghazarian et al.* Clearly, there is no recognition by *Ellington et al.* that an anionic surfactant can be used to reduce ice crystal formation during freezing according to the present invention. Absent a motivation to modify *Ghazarian et al.*, the presently claimed invention would not have been obvious.

Hellemann et al. are apparently relied upon in the outstanding Office Action for the disclosure of sodium laurel sulfate in a composition intended for rabbit semen. See the abstract of *Hellemann et al.* Similar to *Aitken*, *Hellemann et al.* are directed at the use of a composition containing raw egg. It is submitted that one having ordinary skill in the art would not have looked to *Hellemann et al.* for modifying a composition that does not contain raw egg yolk.

Furthermore, the outstanding Office Action fails to provide a sufficient reason to explain why one having ordinary skill in the art would modify *Ghazarian et al.* in view of the disclosure by *Hellemann et al.* to achieve the presently claimed invention.

In view of the comments, the presently claimed invention would not have been obvious from *Ghazarian et al.*, *Saint-Ramon et al.*, *Rajamannan*, *Aitken*, *Ellington et al.*, and *Hellemann et al.* Accordingly, withdrawal of this rejection is requested.

It is believed that this application is in condition for allowance. Early notice to this effect is earnestly solicited.

Respectfully submitted,

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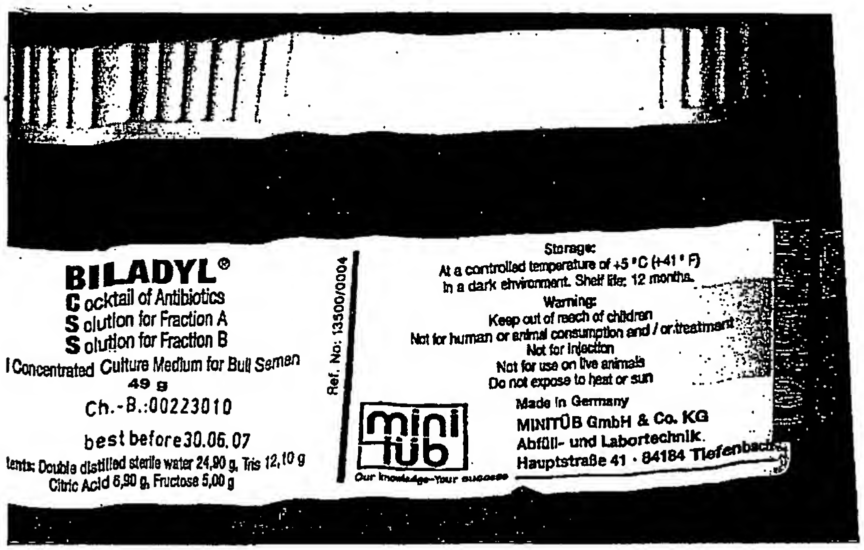
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C ocktail of Antibiotics
S olution for Fraction A
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49 g
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best before30.06.07
Double distilled sterile water 24,90 g, Tris 12,10 g
Citric Acid 6,90 g, Fructose 5,00 g
Ref. No: 13500/0004
Storage:
At a controlled temperature of +5 °C (+41 °F)
In a dark environment. Shelf life: 12 months.
Warning:
Keep out of reach of children
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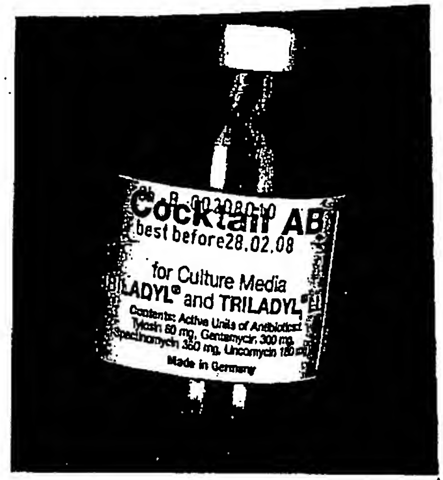
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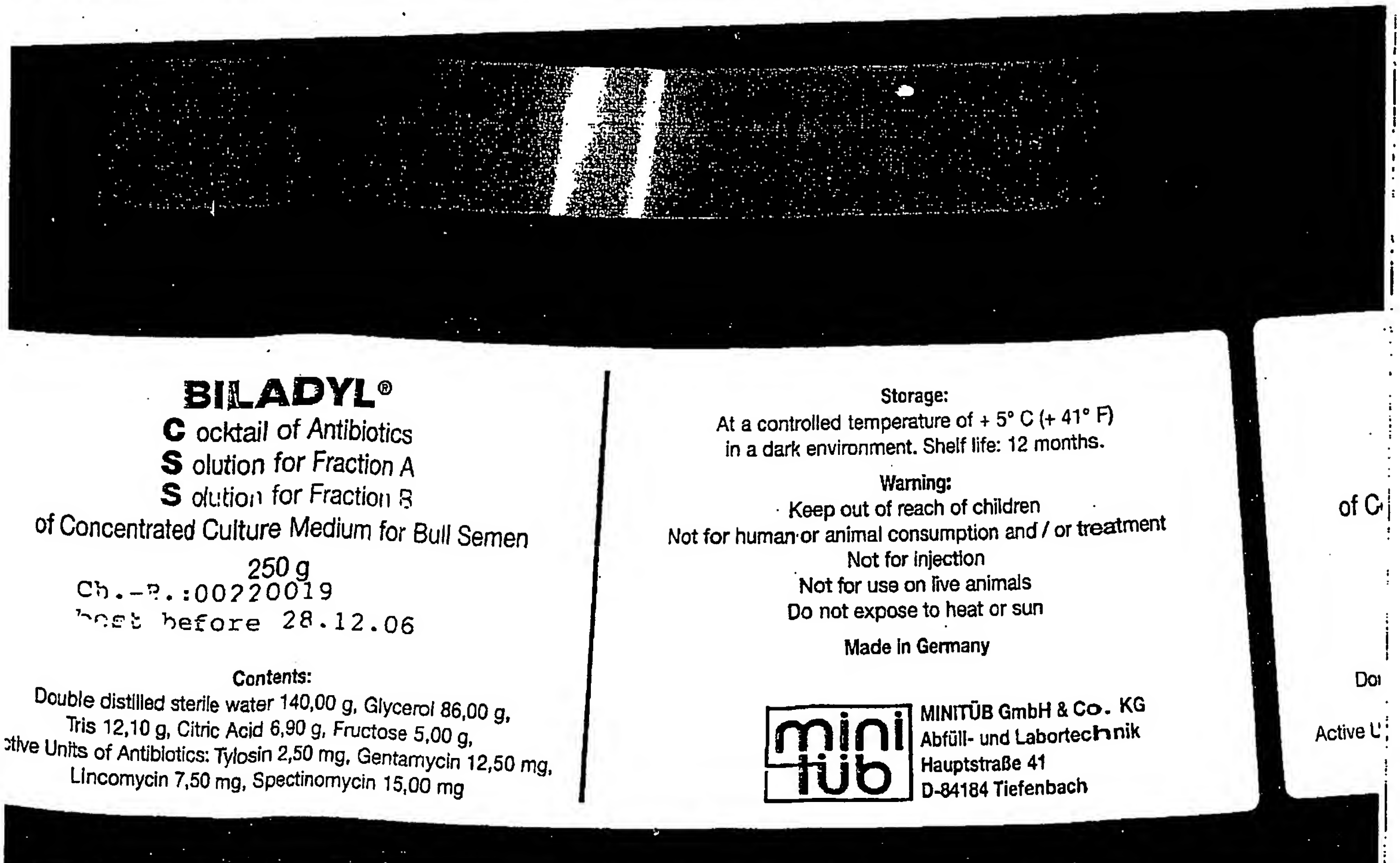
BILADYL®
C ocktail of Antibiotics
S olution for Fraction A
S olution for Fraction B
of Concentrated Culture Medium for Bull Semen
250 g
best before 28.12.06
Contents:
Double distilled sterile water 140,00 g, Glycerol 86,00 g,
Tris 12,10 g, Citric Acid 6,90 g, Fructose 5,00 g,
Units of Antibiotics: Tylosin 2,50 mg, Gentamycin 12,50 mg,
Lincomycin 7,50 mg, Spectinomycin 15,00 mg
Storage:
At a controlled temperature of + 5° C (+ 41° F)
in a dark environment. Shelf life: 12 months.
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Keep out of reach of children
Not for human or animal consumption and / or treatment
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Surfactants and Interfacial Phenomena

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Characteristic Features of Surfactants

Surfactants are among the most versatile of the products of the chemical industry, appearing in such diverse products as the motor oils we use in our automobiles, the pharmaceuticals we take when we are ill, the detergents we use in cleaning our laundry and our homes, the drilling muds used in prospecting for petroleum, and the flotation agents used in benefication of ores. Of late, surfactants have become the subject of intense investigation by researchers in the fields of chemical kinetics and biochemistry because of the unusual properties of the polymeric forms (micelles) of these materials.

In spite of a wealth of experience in the field, the utilization of surfactants for a particular purpose remains more of an art than a science. The objective of this monograph is to attempt to develop a rational approach to this utilization by coupling an appreciation of the characteristics of the various types of surfactants currently available with a knowledge of the chemistry and physics of the phenomena in which they are used to yield an understanding of the reasons for their use for certain purposes and in certain products.

A surface-active agent (or, more briefly, surfactant) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term *interface* indicates a boundary between any two immiscible phases; the term *surface* denotes an interface where one phase is a gas, usually air.

The interfacial free energy is the minimum amount of work required to create that interface. The interfacial free energy per unit

area is what we measure when we determine the interfacial tension between two phases. It is the minimum amount of work required to create unit area of the interface or to expand it by unit area. When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it. When we expand an interface, therefore, the minimum work required to create the additional amount of that interface is the product of the interfacial tension times the increase in area of the interface; $W_{min} = \gamma \times A$. A surface-active agent is therefore a substance that at low concentrations adsorbs at some or all of the interfaces in the system and significantly changes the amount of work required to expand those interfaces. Surfactants usually act to reduce interfacial free energy rather than to increase it, although there are occasions when they are used to increase it.

The questions that immediately arise are the following: Under what conditions can surfactants play a significant role in a process? How does one know when to expect surfactants to be a significant factor in some system under investigation? How and why do they work as they do?

A. Conditions Under Which Interfacial Phenomena and Surfactants Become Significant

During the past few decades it has become recognized that important physical, chemical, and electrical properties of matter confined to phase boundaries are often profoundly different from those of the same matter in bulk. For many systems, even those containing a number of phases, the fraction of the total mass that is localized at phase boundaries (interfaces, surfaces) is so small that the contribution of these "abnormal" properties to the general properties and behavior of the system is negligible. There are, however, many important circumstances under which these "different" properties play a significant, if not a major, role.

One such circumstance is when the phase boundary area is so large relative to the volume of the system that a substantial fraction of the total mass of the system is present at boundaries (e.g., in dispersions of all sorts, such as emulsions, colloids). In this circumstance surfactants can always be expected to play a major role in the system.

Another such circumstance is when the phenomena occurring at phase boundaries are so unusual relative to the expected bulk phase interactions that the entire behavior of the system is determined by

interfacial processes (e.g., heterogeneous catalysis, corrosion, detergency, or flotation). In this circumstance also surface-active agents can play an important role in the process. It is obviously necessary to understand the causes of this abnormal behavior of matter at the interfaces and the variables that affect this behavior in order to predict and control the properties of these systems.

B. General Structural Features and Behavior of Surfactants

The molecules at a surface have higher potential energies than those in the interior. This is because they interact more strongly with the molecules in the interior of the substance than they do with the widely spaced gas molecules above it. Work is therefore required to bring a molecule from the interior to the surface.

Surface-active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an *amphipathic* structure. When a surface-active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant this distortion of the water by the lyophobic (hydrophobic) group of the surfactant, and the resulting increase in the free energy of the system when it is dissolved, means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface. Since less work is now needed to bring molecules to the surface, the presence of the surfactant decreases the work needed to create unit area of surface (the surface free energy or surface tension). On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require desolvation of the hydrophilic group. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the solvent, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structures of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. In a highly polar solvent such

as water, the lyophobic group may be a hydrocarbon or fluorocarbon or siloxane chain of proper length, whereas in a less polar solvent only some of these may be suitable (e.g., fluorocarbon or siloxane chains in polypropylene glycol). In a polar solvent such as water, ionic or highly polar groups may act as lyophilic groups, whereas in a nonpolar solvent such as heptane they may act as lyophobic groups. As the temperature and use conditions (e.g., presence of electrolyte or organic additives) vary, modifications in the structure of the lyophobic and lyophilic groups may become necessary to maintain surface activity at a suitable level. Thus for surface activity in a particular system the surfactant molecule must have a chemical structure that is amphipathic *in that solvent under the conditions of use.*

The hydrophobic group is usually a long-chain hydrocarbon residue, less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as

1. Anionic — the surface-active portion of the molecule bears a negative charge, for example, $RC(=O)O^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).
2. Cationic — the surface-active portion bears a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).
3. Zwitterionic — both positive and negative charges may be present in the surface-active portion, for example, $R\overset{+}{N}H_2CH_2COO^-$ (long-chain amino acid), $R\overset{+}{N}(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).
4. Nonionic — the surface-active portion bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

Differences in the nature of the hydrophobic groups are usually less pronounced than in the nature of the hydrophilic group. Generally, they are long-chain hydrocarbon residues. However, they include such different structures as

1. Straight-chain, long alkyl groups (C_8—C_{20}).
2. Branched-chain, long alkyl groups (C_8—C_{20}).

3. Long-chain (C_8—C_{16}) alkylbenzene residues.
4. Alkylnaphthalene residues (C_3 and greater-length alkyl groups).
5. Rosin derivatives.
6. High-molecular-weight propylene oxide polymers (polyoxypropylene glycol derivatives).
7. Long-chain perfluoroalkyl groups.
8. Polysiloxane groups.

With such a variety of available structures, how does one choose the proper surfactant for a particular purpose? Alternatively, why are only certain surfactants used for a particular purpose, and not other surfactants? Economic factors are often of major importance — unless the cost of using the surfactant is trivial compared to other costs, one usually chooses the most inexpensive surfactant that will do the job. However, this leaves unanswered the question, which of all these different types of surfactants are most likely to do the job? A rational answer to this question, without resorting to time-consuming and expensive trial-and-error experimentation, requires a knowledge of (1) the characteristic features of currently available surfactants (general physical and chemical properties and uses), (2) the interfacial phenomena involved in the job to be done and the role of the surfactant in these phenomena, (3) the surface chemical properties of various structural types of surfactants and the relationship of the structure of a surfactant to its behavior in various interfacial phenomena. The following chapters attempt to cover these areas.

I. CHARACTERISTIC FEATURES AND USES OF COMMERCIALLY AVAILABLE SURFACTANTS

A. Anionics (~73% of U.S. Consumption of Surfactants)*

1. Carboxylic Acid Salts

Sodium and Potassium Salts of Straight-Chain Fatty Acids (Soaps), ~25% of U.S. Consumption

Properties: Below 10 carbons, too soluble for surface activity; above 20 carbons (straight chain), too insoluble for use in aqueous medium,

*Consumption figures from D. H. Scharer, J. G. Moffett, and H. Stupel, paper presented before Chemical Specialties Manufacturers Assoc., Dec. 3, 1973, Washington, D.C.; D. H. von Hennig, paper presented at Chemical Industry Assoc. Workshop meeting, Absecon, N.J., June 14, 1976.

but usable for nonaqueous systems (e.g., detergents in lubricating oils or dry-cleaning solvents).

Advantages: Easily prepared by neutralization of free fatty acids or saponification of triglycerides in simple equipment. Can be made in situ (e.g., for use as emulsifying agent) (1) by adding fatty acid to oil phase and alkaline material to aqueous phase or (2) by partial saponification of triglyceride oil. Excellent physical properties for use in toilet soap bars.

Disadvantages: (1) Form water-insoluble soaps with divalent and trivalent metallic ions, (2) insolubilized readily by electrolytes, such as NaCl, (3) unstable at pH below 7, yielding water-insoluble, free fatty acid.

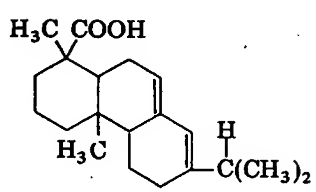
Major types and their uses: Sodium salts of tallow (animal fat) acids. (Tallow acids are oleic, 40—45%; palmitic, 25—30%; stearic, 15—20%.) Used in toilet soap bars and for degumming of silk, where alkaline solution is required. For industrial use in hard water, lime soap-dispersing agents (sulfonates and sulfates) are added to prevent precipitation of insoluble lime soaps.

Sodium and Potassium Salts of Coconut Oil Fatty Acids

(Coconut fatty acids are C_{12}, 45—50%; C_{14}, 16—20%; C_{16}, 8—10%; oleic, 5—6%; $<C_{12}$, 10—15%). Used as electrolyte-resistant soaps (sea water washing) and in liquid soaps, especially as the potassium soaps.

Sodium and Potassium Salts of Tall Oil Acids

(Tall oil, a byproduct of paper manufacture, is a mixture of fatty acids and rosin acids from wood; 50—70% fatty acid, mainly oleic and linoleic, 30—50% rosin acids related to abietic acid,



the main constituent of rosin). Mainly "captive" use or in situ preparation for various industrial cleaning operations.

Advantages: Inexpensive. More water-soluble and hard-water resistant than tallow soaps. Lower viscosity solutions than tallow soaps at high concentrations, better wetting.

Soaps of synthetic long-chain fatty acids are produced in Europe, but not in the United States at present.

Amine Salts

Triethanolamine salts are used in nonaqueous solvents and in situ preparation as an emulsifying agent (free fatty acid in oil phase, triethanolamine in aqueous phase). Ammonia, morpholine, and other volatile amine salts — used in polishes, where evaporation of the amine following hydrolysis of the salt leaves only water-resistant material in film.

Other Types

N-Lauroyl sarcoside, $RCON(CH_3)CH_2COO^-Na^+$. Toothpaste ingredient, since nontoxic, strongly foaming, and enzyme-inhibiting. Good detergency (like soap) and has advantage of being less sensitive to hard water and acids than the usual soap. Nonirritating to skin.

Acylated Polypeptides

(From partially hydrolyzed protein from scrap leather and other waste protein.) Used in hair preparations and shampoos, alkaline cleaning preparations, wax strippers. Good detergency and resistance to hard water.

Advantages: Soluble in concentrated aqueous solutions of alkaline salts. Nonirritating to skin; reduces skin irritation produced by other surfactants (e.g., sodium lauryl sulfate). Substantive to hair. Imparts soft "hand" to textiles.

Disadvantages: Precipitated by high concentrations of Ca^{++} or Mg^{++}, acids (below pH 5). Lower foaming than lauryl sulfates. Requires foam booster (e.g., alkanolamides) when foaming is important.

2. Sulfonic Acid Salts (26% of U.S. Consumption)*

Linear Alkylbenzenesulfonates (LAS)

Random distribution of benzene ring along linear chain. Mainly sodium salt, but also calcium salt (which may be oil-soluble or dispersible) and amine salts, which are also organic solvent soluble or dispersible. The chain length of the alkyl portions is about 12 carbons in most cases. Relatively cheap, but requires acid-resistant equipment for manufacture and sophisticated SO_3 sulfonation

*See footnote, p. 5.

equipment for large-scale production. Small-scale manufacture can be done with oleum ($H_2SO_4 + SO_3$). Major amounts sold as free sulfonic acid for neutralization (by processors) with amines. The sodium salt is the most widely used surfactant in industrial and high-foaming household detergents. The triethanolamine salt is used in liquid detergents and cosmetics; the isopropylamine salt in dry cleaning, since it is hydrocarbon-soluble; and the dimethylamine salt in agricultural emulsions and dry-cleaning solvents (to solubilize the water used to remove water-soluble stains).

Advantages: Completely ionized, water-soluble, free sulfonic acid; therefore solubility is not affected by low pH. Calcium and magnesium salts are water-soluble, and therefore not affected by hard water. Sodium salt is sufficiently soluble in the presence of electrolyte (NaCl, Na_2SO_4) for most uses. Resistant to hydrolysis in hot acid or alkali.

Disadvantages: Sodium salt is not soluble in organic solvents, except alcohols. Even linear dodecylbenzenesulfonate is resistant to biodegradation under anaerobic conditions, although it is degradable under aerobic conditions.

Higher Alkylbenzenesulfonates

Prepared with longer-chain olefins (C_{13}—C_{15}), are more oil-soluble, and are useful as lubricating oil additives.

Benzene-, Toluene-, Xylene-, and Cumenesulfonate

Mainly sodium xylenesulfonate, are used for increasing the solubility of LAS in aqueous formulations (hydrotropic agents). They thin soap gels and detergent slurries and solubilize water-insoluble polar ingredients (phenols) in aqueous formulations.

Ligninsulfonates

These are a byproduct of paper manufacture, prepared mainly as sodium and calcium salts, but to some extent also as ammonium salts. They are used as dispersing agents for solids and o/w emulsion stabilizers. They are sulfonated polymers of molecular weight 1,000—20,000 of complex structure containing free phenolic, primary and secondary alcoholic, and carboxylate groupings. The sulfonate groups are at the α- and β-positions of C_3 alkyl groups joining the phenolic structures. They reduce the viscosity of and stabilize aqueous slurries of dyestuffs, pesticides, and cement.

Advantages: They are among the most inexpensive surfactants and are available in very large quantities. They produce very little foam during use.

Disadvantages: Very dark color, soluble in water but insoluble in organic solvents, including alcohol. They produce no significant surface tension lowering.

Petroleum Sulfonates

Products of the refining of selected petroleum fractions with concentrated sulfuric acid or oleum, in the production of white oils. Metal or ammonium salts of sulfonated complex cycloaliphatic hydrocarbons.

Uses: Tertiary oil recovery. Sodium salts of lower molecular weight (~435—450) are used as o/w emulsifying agents in soluble metal cutting oils, frothing agents in ore flotation, components of dry-cleaning soaps; sodium salts of higher molecular weight (465—500) are used as rust preventatives and pigment dispersants in organic solvents. Ammonium salts are used as ashless rust inhibitors and soluble dispersants in fuel oils and gasoline. Mg, Ca, and Ba salts are used as sludge dispersants for fuel oils and as corrosion inhibitors for diesel lubricating oils.

Advantages: Inexpensive.

Disadvantages: Dark in color. May contain unsulfonated hydrocarbon.

N-Acyl-n-Alkyltaurates, $RCON(R')CH_2CH_2SO_3^-M^+$

The solubility, foaming, detergency, and dispersing powers of the *N*-methyl derivatives are similar to those of the corresponding fatty acid soaps in soft water, but these materials are effective both in hard and soft water, are not sensitive to low pH, and are better wetting agents. They show good stability to hydrolysis by acids and alkali, good skin compatibility, and good lime soap-dispersing power.

Uses: In bubble baths (together with soap) and in toilet bars together with soap, since they show no decrease in foaming or lathering in combination with the latter (in contrast with other anionics). In alkaline bottle washing compounds and for seawater laundering, since their Ca and Mg salts are soluble, even in water containing high electrolyte concentrations. Impart soft feel ("hand") to fibers and fabrics (similar to soaps and fatty alcohol sulfates, in contrast with nonionics and alkylarylsulfonates). Wetting and dispersing agent in wettable pesticide powders.

Paraffin Sulfonates (SAS), Secondary n-Alkanesulfonates

Produced in Europe by sulfoxidation of *n*-paraffin hydrocarbons separated from refinery product streams (e.g., by molecular sieves) with SO_2 and O_2 in the presence of ultraviolet light.

Uses: In detergents, similar to LAS. Unpurified paraffin sulfonates, containing about 50% paraffin, are used in fat liquoring of leather.

Advantages: Solubility in water is reported to be somewhat better, viscosity of aqueous solutions somewhat lower, skin compatability somewhat better, and biodegradability at low temperature somewhat better than that of LAS of comparable chain length.*

α-Olefin Sulfonates (AOS)

Produced by reaction of SO_3 with linear α-olefins. Product is a mixture of alkenesulfonates and hydroxyalkanesulfonates (mainly 3- and 4-hydroxy). This is a new type of surfactant now being introduced into light-duty liquid detergents in the United States.

Advantages: Reported to be somewhat more biodegradable than LAS; less irritating to the skin.**

Sulfosuccinate Esters, $ROOCCH_2CH(SO_3^-M^+)COOR$

Used as wetting agents for paints, printing inks, textiles, agricultural emulsions, and so on. The dioctyl(2-ethylhexyl) ester is soluble in both water and organic solvents, including hydrocarbons, and is therefore used in dry-cleaning solvents.

Advantages: Can be produced electrolyte-free, and is thus completely soluble in organic solvents and usable where electrolyte must be avoided.

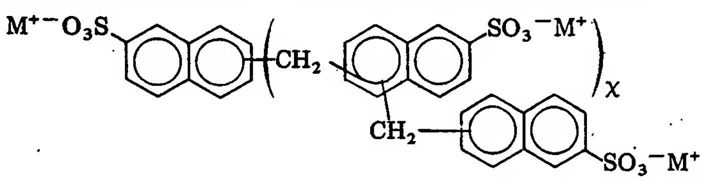
Disadvantages: Hydrolyzed by hot alkaline and acidic solutions.

Alkylnaphthalenesulfonates

Mainly butyl- and isopropylnaphthalenesulfonates, for use as wetting agents for powders (agricultural wettables, powdered pesticides). Also used as wetting agents in paint formulations.

Advantages: Available in nonhygroscopic powder form for mixing into formulated powders.

Naphthalenesulfonic acid—formaldehyde condensates,



$x = 0$–4

*G. H. Taeuber, paper presented at American Oil Chemists Society short course, Lake Placid, N.Y., June 15, 1971.

**W. J. DeWitt, paper presented at American Oil Chemists Society short course, Lake Placid, N.Y., June 15, 1971.

Uses: Similar to those for ligninsulfonates (dispersing agents for solids in aqueous media, grading aids for solids). Advantages over the usual ligninsulfonates are lighter color, even less foam.

Isethionates, $RCOOCH_2CH_2SO_3^-M^+$

Used in cosmetic preparations, synthetic toilet soap bars.

Advantages: Excellent detergency and wetting power, good lime soap dispersing power, good foaming power.

Disadvantages: Hydrolyzed by hot alkali.

3. Sulfuric Acid Ester Salts

*Sulfated Linear Primary Alcohols (~6% of U.S. Consumption)**

Sulfated "coconut alcohol" from hydrogenation of coconut oil (see composition under carboxylic acid salts) — mainly C_{12}, or sulfated "tallow alcohols" (see composition under carboxylic acid salts) — mainly oleyl, or sulfated synthetic alcohols from linear olefins to match these two types.

Advantages: Easily produced from alcohol and $ClSO_3H$ in neighborhood of room temperature in relatively simple equipment to yield very light-colored product. Also produced by thin film sulfation with SO_3 vapor. Excellent foaming properties, especially if some unsulfated alcohol is retained in product. Sulfated lauryl alcohol retains its excellent foaming properties even in hard water. Coconut alcohol derivative is suitable for food or pharmaceutical use.

Disadvantages: Hydrolyzed readily in hot acidic medium

Types available and their use: Na salts are most common. Na "lauryl" sulfate used in low-temperature detergents for delicate fabrics, dyeing "retarder" when amino groups are present on the fiber, toothpaste detergent, food and cosmetic emulsions, dyestuff dispersion in aqueous medium. Mg "lauryl" sulfate used where a less hygroscopic powder is needed; has increased solubility over Na salt in hard water and higher alkali tolerance.

Sulfated C_{16}—C_{20} primary alcohol used together with LAS in some high-foaming household detergents. Diethanolamine, triethanolamine, and ammonia salts are used in hair shampoos and cosmetics, where their higher solubility in water and their slightly acidic pH makes them desirable (latter makes hair more manageable).

Sulfated Polyoxyethylenated Straight-Chain Alcohols (~6% of U.S. Consumption).

$R(OC_2H_4)_xSO_4^-M^+$ ($x = 3$, usually).

Advantages over unethenoxylated sulfated alcohols: More water-

*See footnote, p. 5.

soluble, more electrolyte resistant, much better lime soap dispersing agents, foam more resistant to water hardness and protein soil. NH_4 salt is less irritating to skin and eyes, produces higher viscosity solutions (advantages in shampoos).

Uses: In light-duty liquid detergents to improve foaming characteristics; together with nonionic in heavy-duty liquids (free of phosphates); in shampoos.

Sulfated Triglyceride Oils (Sulf[on]ated Oils)

Produced by sulfation of hydroxy group and/or double bond in fatty acid portion of the triglyceride. (Iodine values of triglycerides used range from 40 to 140.) Mainly castor oil used (fatty acid present is mainly 12-hydroxyoleic acid), but also fish oils, tallow, sperm oil (25% oleyl, 50% C_{16} saturated fatty acid, remainder saturated C_{18} and C_{16} unsaturated). First synthetic surface-active agent (1850). Mainly used as textile wetting, cleaning, and finishing agent. Also used as emulsifying agent in textile finishing and in metal cutting oils. Liquoring compositions for leather.

Advantages: Cheap, easy to produce near room temperature by mixing oil and concentrated H_2SO_4. Product is a complex mixture since hydrolysis to sulfated di- and monoglycerides, and even free fatty acid, occurs during manufacture, and even sulfonation occurs to slight extent (in alpha position of fatty acid), yielding a wide range of properties. Adsorbs onto fibers to yield soft "hand." Produces very little foam and also decreases foaming of other surfactants.

Disadvantages: Readily hydrolyzed in hot acidic or hot alkaline solutions.

4. Phosphoric and Polyphosphoric Acid Esters

Mainly phosphated polyoxyethylenated long-chain alcohols and phenols, some sodium alkyl phosphates (not oxyethylenated). The polyoxyethylenated materials are available in free acid form or as Na or amine salts. Products are mixtures of monobasic and dibasic phosphates.

Advantages: The free acids have good solubility in both water and organic solvents, including some hydrocarbon solvents, and can be used in free acid form since acidity is comparable to that of phosphoric acid. Low foaming. Not hydrolyzed by hot alkali; color unaffected. Polyoxyethylenated materials show good resistance to hard water and concentrated electrolyte.

Disadvantages: Only moderate surface activity as wetting, foaming, or washing agents. Somewhat more expensive than sulfonates. Na salts usually not soluble in hydrocarbon solvents.

Uses: Mainly as emulsifying agents in agricultural emulsions (pesticides, herbicides), especially those blended with concentrated liquid fertilizer solutions, where emulsion stability in presence of high electrolyte concentration is required. Dry-cleaning detergents.

5. Perfluorinated Anionics

Perfluorocarboxylic acids are much more completely ionized than fatty acids, hence are unaffected in aqueous solution by acids or polyvalent cations. They show good resistance to strong acids and bases, reducing and oxidizing agents, and heat (in excess of 600°F in some cases). They are much more surface active than the corresponding carboxylic acids and can reduce the surface tension of water to much lower values than are obtainable with surfactants containing hydrocarbon groups. They are also surface active in organic solvents. Perfluoroalkyl sulfonates, too, have outstanding chemical and thermal stability.

Uses: Emulsifiers for aqueous lattices of fluorinated monomers. Suppression of chromic acid mist and spray from chromium plating baths. "Light water" control of oil and gasoline fires. Formation of surfaces that are both hydrophobic and oleophobic on textiles, paper, and leather. Inhibition of evaporation of volatile organic solvents.

Disadvantages: Much more expensive than other types of surfactants, resistant to biodegradation even when straight-chain.

B. Cationics (~6% of U.S. Consumption of Surfactants)*

Advantages: Compatible with nonionics and zwitterionics. Surface-active moiety has a positive charge, thus adsorbs strongly onto most solid surfaces (which are usually negatively charged), and can impart special characteristics to the substrate. Some examples are given in Table 1-1. This adsorption also makes possible the formation of emulsions that "break" in contact with negatively charged substrates, allowing deposition of active phase onto substrate.

Disadvantages: Most types are not compatible with anionics (amine oxides are an exception). Generally, more expensive than anionics or nonionics. Show poor detergency, only poor suspending power for carbon.

*See footnote, p. 5.

Table 1-1. Some Uses of Cationics Resulting From Their Adsorption onto Solid Substrates[a]

Substrate	*Use*
Natural and synthetic fibers	Fabric softeners Antistatics Textiles auxiliaries
Fertilizers	Anticaking agents
Weeds	Herbicides
Aggregates	Adhesion promoters in asphalt
Metals	Corrosion inhibitors
Pigments	Dispersants
Plastics	Antistatics
Skin, keratin	Toiletries, hair conditioners
Ores	Flotation agents
Microorganisms	Germicides

[a]M. K. Schwitzer, *Chemistry and Industry*, 822 (1972).

1. **Long-Chain Amines and Their Salts**

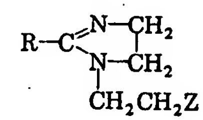
Primary amines derived from animal and vegetable fatty acids, tall oil, synthetic C_{12}—C_{18} primary, secondary, or tertiary amines. Adsorb strongly onto most surfaces, which are usually negatively charged. Very soluble and stable in strongly acidic solutions. Sensitive to pH changes — become uncharged and insoluble in water at pH above 7.

Uses: Cationic emulsifying agents at pH below 7. Corrosion inhibitors for metal surfaces, to protect them from water, salts, acids. Saturated, very long-chain amines best for this purpose, since these give close-packed hydrophobic surface films. Used in fuel and lubricating oils to prevent corrosion of metal containers. Anticaking agents for fertilizers, adhesion promotors for painting damp surfaces. Ore flotation collectors, forming nonwetting films on specific minerals, allowing them to be separated from other ores.

Disadvantages: Poor leveling is characteristic of cationic wax or wax-resin emulsions.

2. Diamines and Polyamines and Their Salts

Uses and properties similar to above; main use as adhesion promotors for asphalt coating of wet or damp road surfaces; *N*-alkyltrimethylenediamine salts used in cosmetic emulsions; *N*-alkylimidazolines



are used as textile fabric softeners (no yellowing on aging) to give smooth "hand" and as adhesion promotors for asphalt coating of wet or damp road surfaces.

Other uses: Ore flotation, to produce hydrophobic surface on ore or impurities; pigment coating, to make hydrophilic pigment lipophilic (adsorbed diamine salt yields positively charged surface, which then adsorbs fatty acid anion to give strongly chemisorbed lipophilic monolayer).

3. Quaternary Ammonium Salts (1 + % of U.S. Consumption)*

N-Alkyltrimethylammonium chlorides or *N*,*N*-dialkyldimethylammonium chlorides, mainly.

Advantages: Unaffected by pH changes — positive charge remains in acidic, neutral, and alkaline media.

Disadvantages: Since water solubility is retained at all pHs, they are more easily removed from surfaces onto which they may be adsorbed (insolubility of nonquaternary amines in water at pH above 7 is often an advantage).

Uses: Bis (hydrogenated tallow alkyl) dimethylammonium chloride used as textile softener industrially and for home use in final rinse in washing machine. Imparts fluffy, soft "hand" to fabrics by adsorbing onto them with hydrophobic groups oriented away from fiber. *N*-Alkyltrimethylammonium chlorides used as emulsifying agents for acidic emulsions or where adsorption of emulsifying agent onto substrate is desirable (e.g., in insecticidal emulsions, adsorption of emulsifying agent onto substrate breaks emulsion and releases active ingredient as water-insoluble material). Highly effective germicides for industrial use. [Bis (long-chain alkyl) derivatives are less effective than monoalkyls; oxyethylenation drastically reduces germicidal effect, chlorinated aromatic ring increases it.]

*See footnote, p. 5.

N-Benzyl-*N*-alkyldimethylammonium halides are used as germicides, disinfectants, sanitizers. They are compatible with alkaline inorganic salts and nonionics and are used together with them in detergent-sanitizers for public dishwashing (restaurants, bars). They are also used as hair conditioners (aftershampoo rinses), since they adsorb onto hair, imparting softness and antistatic properties. The cetyl derivative is used in oral antiseptics.

4. **Polyoxyethylenated Long-Chain Amines**

$RN[(CH_2CH_2O)_xH]_2$. Combine increased water solubility imparted by polyoxyethylene chains with cationic characteristics of the amino group. As the oxyethylene content increases, cationic properties decrease and materials become more like nonionics in nature (e.g., solubility in water does not change much with pH change; incompatibility with anionics diminishes). If oxyethylene content is high enough, materials do not require acidic solution for water solubility.

Uses: In production of xanthate rayon to improve tensile strength of regenerated cellulose filaments and to keep spinnerets free of incrustations. Emulsifying agents for herbicides, insecticides, polishes, and wax emulsions, which "break" on contact with the substrate and deposit the oil phase on it.

Advantages: Salts with inorganic or low molecular weight organic acids are water-soluble, those with high molecular weight organic acids are oil-soluble, even when the free polyoxyethylenated amines are oil-insoluble. Show inverse solubility in water on heating, like other polyoxyethylene derivatives.

5. **Quaternized Polyoxyethylenated Long-Chain Amines**

$RN(CH_3)[(C_2H_4O)_xH]_2^+Cl^-$. Used as textile antistatic agents (ionic charge dissipates static charge; polyethylene group adsorbs water, which also dissipates charge). Also used as dyeing levelers (retarders) by competing transiently for dye sites on fabrics during the dyeing process, thereby decreasing the rate of dyeing at its most active sites — where they are most rapidly adsorbed — to that of the less active sites. This causes more uniform dyeing. Used as corrosion inhibitors for metallic surfaces. Promote adhesion in asphalt (by adsorption to form hydrophobic, oleophilic surface film on substrate). Dispersing agents for clay in greases, emulsifying agents for polar compounds (e.g., fatty acids and amines) in o/w emulsions. Trifluoroacetate salts are used to produce foam that

reduces chromic acid spray and mist in chromium plating. $(RCONH(CH_2)_3N(CH_3)_2CH_2CH_2OH]^+NO_3^-$ is used as a surface or internal antistatic for plastics.

6. **Amine Oxides (1 + % of U.S. Consumption)***

Usually, *N*-alkyldimethylamine oxides. Form 1:1 salts with anionics that are much more surface-active than either the anionic or the amine oxide. Used as foam stabilizer for LAS and other anionics in detergents, liquid dishwashing compounds, and shampoos. Also increase the viscosity of the shampoo and managability of hair.

Advantage over alkanolamide foam stabilizers: Effective at lower concentrations.

C. Nonionics (~21% of U.S. Consumption)*

Advantages: Compatible with all other types of surfactants. Generally available as 100% active material free of electrolyte. Can be made resistant to hard water, polyvalent metallic cations, electrolyte at high concentration; soluble in water and organic solvants, including hydrocarbons. Polyoxyethylenated nonionics are generally excellent dispersing agents for carbon.

Disadvantages: Products are liquids or pastes, rarely nontacky solids. Poor foamers (may be advantage sometimes); no electrical effects (e.g., no strong adsorption onto charged surfaces). Ethylene oxide derivatives show inverse temperature effect on solubility in water, may become insoluble in water on heating.

1. **Polyoxyethylenated Alkylphenols, Alkylphenol Ethoxylates (~6% of U.S. Consumption)***

Mainly polyoxyethylenated *p*-nonylphenol, *p*-octylphenol, or *p*-dodecylphenol (sometimes, dinonylphenol), derived from disobutylene, propylene trimer, or propylene tetramer.

Advantages: Length of alkyl group on phenol or polyoxyethylene chain can be varied to give range of products varying in solubility from water-insoluble, aliphatic hydrocarbon-soluble products (1–5 moles of ethylene oxide) to water-miscible, aliphatic hydrocarbon-insoluble ones. Polyoxyethylene linkages stable to hot dilute acid, alkali (except for some yellowing in the latter), and oxidizing agents

*See footnote, p. 5.

such as hypochlorite, peroxide, or perborate. Antistatic properties resulting from hydratable multiple ether linkages. Advantage over polyoxyethylenated alcohols in that there is never any free alkylphenol in oxyethylenated product, since phenolic OH is more reactive than alcohol OH. Thus no toxicity or dermatology problems associated with free phenol or other problems associated with presence of free hydrophobe.

Disadvantages: More resistant to biodegradation than other nonionic types.

Uses: Mainly industrial, because of low degradability. Water-insoluble types used for w/o emulsifying agents, foam control agents, cosolvents; water-soluble types for o/w emulsifying agents for paints, agricultural emulsions, miscellaneous industrial and cosmetic emulsions. Materials with high ethylene oxide content (>15 moles of ethylene oxide) are used as detergents and emulsifiers in strong electrolyte systems and as foam entrainment agents in concrete. Also used in liquid detergents and as dyeing retarders for cellulose (surfactant forms complex with dye molecules). Excellent dispersing agents for carbon.

2. Polyoxyethylenated Straight-Chain Alcohols, Alcohol Ethoxylates (~9% of U.S. Consumption)*

Mainly mixed coconut oil-derived, tallow-derived, and synthetic straight-chain alcohols are used as the hydrophobes, both primary and random secondary. Oleyl derivatives are more fluid than saturated alcohol derivatives; lubricating properties are more pronounced in the saturated alcohol derivatives than in the unsaturated ones. Uses for industrial purposes similar to those of polyoxyethylenated alkyl phenols. In low and controlled foam laundrv detergents.

Advantages: More easily biodegraded than alkylphenol ethoxylates, more resistant to hydrolysis in hot alkaline solutions than polyoxyethylenated fatty acids, more water-soluble and better wetting powers than corresponding fatty acid ethoxylates. Somewhat better than the corresponding alkylphenol ethoxylates for emulsification. More water-soluble than LAS, for use in high active, heavy-duty liquid detergents free of phosphates. More effective detergency than LAS under cool washing conditions and on synthetic fabrics.

Disadvantages: Contain appreciable amounts of nonoxyethylenated hydrophobe.

*See footnote, p. 5.

3. Polyoxyethylenated Polyoxypropylene Glycols

Made solely from ethylene oxide and propylene oxide. Materials with low ethyleneoxide content have very little foam; materials of high molecular weight with low ethylene oxide content are wetting agents. Materials with high ethylene oxide content are dispersing agents. Products range in molecular weight from 1000 to 30,000.

Uses: High molecular weight materials with high ethylene oxide content are used as dispersants for pigments in latex paints or for scale removal in boilers; low molecular weight materials with low ethylene oxide content are used as foam control agents in laundry detergents and in rinsing aids for dishwashing.

Advantages: Both hydrophobic group $\leftarrow CH_2CH(CH_3)O \rightarrow_x$ and hydrophilic group $\leftarrow CH_2CH_2O \rightarrow_y$ can be varied at will to "tailor-make" product with specific properties. Products with high molecular weight hydrophobes and high ethylene oxide contents are nontacky solids (in contrast to other polyoxyethylenated nonionics). Better wetting agents than ester-type nonionics.

4. Polyoxyethylenated Mercaptans

Unstable to oxidizing agents, such as chlorine, hypochlorites, peroxides, and strong acids. (This may be an advantage when inactivation of surfactant after use is desired.) Stable in hot, strong alkali. Good lime soap dispersants.

Uses: Textile detergents (cleaning and scouring of wool), metal cleaning, shampoos.

Advantages: Some evidence that quaternary ammonium compounds are more effective as detergent sanitizers when formulated with polyoxyethylenated mercaptans rather than with other polyoxyethylenated nonionics.

Disadvantages: Have slight, unpleasant odor that is difficult to mask.

5. Long-Chain Carboxylic Acid Esters

Advantages: In some cases, very easily made in simple equipment. Outstanding emulsifying properties, compared to other nonionic types.

Disadvantages: Readily hydrolyzed by hot acids or hot alkalies. Lower foam than other nonionic types (may be advantage for some uses).

Glyceryl and Polyglyceryl Esters of Natural Fatty Acids

Advantages: Easily made by glycerolysis of triglycerides or, somewhat more expensively, by esterification of fatty acids with

glycerol in simple equipment. Edible, hence usable in food and pharmaceutical products. May be liquid, soft plastic, or hard wax, depending on fatty acid composition. Can be modified by reaction with acetic, lactic, or tartaric acids.

Disadvantages: Mixture of mono- and diglycerides (glycerides of ~90% monoester content must be made by distillation of usual reaction product).

Uses: Cosmetic emulsifiers, food emulsifiers for bread, ice cream, margarine, synthetic cream, and other dairy products.

Propylene Glycol, Sorbitol, and Polyoxyethylenated Sorbitol Esters

Propylene glycol esters are more lipophilic than the corresponding glycerol esters; sorbitol esters are more hydrophilic (unless dehydrated in course of manufacture). Polyoxyethylenation of sorbitol (and anhydrosorbitol produced during manufacture) gives wide range of solubilities and hydrophilic-lipophilic balances to products.

Advantages: Edible, thus useful for food and drug use (e.g., soluble vitamins).

Uses: Food and pharmaceutical emulsifiers.

Polyoxyethylene Glycol Esters and Polyoxyethylenated Fatty Acids (Including Tall Oil)

Prepared either by esterification of polyoxyethylene glycol with fatty acid or by addition of ethylene oxide to fatty acid. Former type is more easily made, but is a mixture of mono- and diesters. Tall oil derivatives have lower foaming properties than corresponding fatty acid derivatives. Advantage over glyceryl esters in that length of hydrophilic group, and hence solubility and hydrophilic-lipophilic balance of product, can be varied as desired. Generally better emulsifying agents than polyoxyethylenated alcohols or alkyl phenols.

Disadvantages: Generally poor wetting properties; hydrolyzed by hot alkaline solutions.

Uses: Emulsification of all sorts, except where hot alkaline solutions are encountered.

6. Alkanolamine "Condensates," Alkanolamides (~3% of U.S. Consumption)*

Mainly of diethanolamine or monoisopropanolamine. Good stability to hydrolysis by hot alkali, poor-fair stability to hot acids.

*See footnote, p. 5.

1:1 Alkanolamine—Fatty Acid "Condensates"

Made by reaction of methyl ester of fatty acid with equimolar amount of alkanolamine (about 90% alkanolamide content in product). Mainly based on coconut fatty acid or purified coconut (lauric) acid.

Diethanolamide is insoluble, but dispersible, in water, soluble in organic solvents except some aliphatic hydrocarbons. Compatible with both anionics and cationics over wide pH range. Poor wetting and detergent properties, but synergistic to surfactants showing these properties. Shows corrosion-inhibiting properties for steel. Easily prepared.

Uses: Foam stabilizers for LAS in laundry and dishwashing detergents (alternative to amine oxides). Thickeners for liquid detergents and shampoos (containing sodium lauryl sulfate).

2:1 Alkanolamine—Fatty Acid "Condensates"

Made by reaction of 2 moles of alkanolamine with 1 mole of free fatty acid. Contains about 60—70% alkanolamide, 25—30% alkanolamine, 3—5% fatty acid (as soap of alkanolamine). Mainly based on coconut fatty acid.

Advantages over 1:1 condensate: Diethanolamine-coconut fatty acid "condensate" is soluble in both water and organic solvents except aliphatic hydrocarbons. Excellent detergent, emulsifier, and viscosity thickener in aqueous medium at low concentrations.

Disadvantages: Complex mixture, foam stabilization depends only on amide content (60—70%). Fatty acid content makes it incompatible with cationics.

Uses: Textile detergent, shampoo ingredient, emulsifying agent, rust inhibitor, dry-cleaning soap, fuel oil additive.

7. Tertiary Acetylenic Glycols, $R_1R_2C(OH)C{\equiv}C\,C(OH)R_1R_2$

Advantages: Excellent wetting agents at low concentrations, nonfoaming. Nonwaxy solids (rare among nonionics). Volatile with steam, thus readily removed from system after use.

Disadvantages: Very low solubility in water, decompose in acidic medium, relatively expensive. Polyoxyethylenation of each hydroxyl group with 4—9 oxyethylene units increases solubility in water without significant change in surface properties, but products are liquids and nonvolatile with steam.

Uses: Wetting agents for use in powdered solids (dyestuffs, wettable pesticide powders); synergist with anionics and nonionics to decrease foam, reduce viscosity, and increase wetting in aqueous solution; rinse aids in dishwashing; wetting agents in emulsion paints.

D. Zwitterionics (<1% of U.S. Consumption)*

Advantages: Compatible with all other types of surfactants. Less irritating to skin and eyes than other types. May be adsorbed onto negatively or positively charged surfaces without forming hydrophobic film.

Disadvantages: Often insoluble in most organic solvents, including ethanol.

1. pH-Sensitive Zwitterionics

These are ampholytic materials, which show the properties of anionics at high pHs and those of cationics at low pHs. In the vicinity of their isoelectric points they exist mainly as zwitterionics and show minimum solubility in water, and minimum foaming, wetting, and detergency.

β-N-Alkylaminopropionic Acids, $R\overset{+}{N}H_2CHCH_2COO^-$

Isoelectric point at pH ~ 4. Very soluble in aqueous solutions of strong acids and alkalies, even in the presence of electrolytes like NaCl. Solubility is low in most organic solvents, including ethanol and isopropyl alcohol. Adsorb from aqueous solution onto skin, textiles, fibers, and metals. On hair and textile fibers they confer lubricity, softness, and antistatic properties; on metals they act as corrosion inhibitors. They solubilize many organic and inorganic compounds (e.g., quaternary ammonium salts, phenols, polyphosphates) in aqueous solutions. Effective emulsifying agents for long-chain alcohols and slightly polar compounds, not good for paraffinic oils. Emulsions can be converted from anionic to cationic by pH adjustment. Emulsions more easily prepared at alkaline than at acidic pHs. *N*-Dodecyl derivative is an excellent wetting agent and foam producer at alkaline pHs, less of a foamer at acid pHs.

Uses: Bactericides, corrosion inhibitors, pigment dispersion aids, cosmetics, alkaline cleaners with high alkali and electrolyte content.

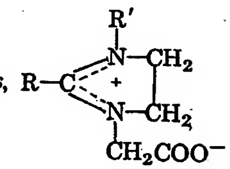
N-*Alkyl-β-iminodipropionic acids,* $R\overset{+}{N}H\begin{matrix}\diagup CH_2COO^- \\ \diagdown CH_2COOH\end{matrix}$

Isoelectric point, pH = 1.7—3.5. More soluble in water than corresponding monopropionic acid derivatives. Show very low order of skin and eye irritation. May be removed from substrates onto

*See footnote, p. 5.

which they have adsorbed at pHs below their isoelectric points by raising the pH.

Uses: Fabric softeners.

Imidazoline carboxylates, 

R from RCOOH of commercially available fatty acids: When R′ is H they are ampholytic and show cationic properties at low pHs, anionic properties at high pHs. When R′ = CH_2Z, pH sensitivity is more closely related to that of *N*-alkylbetaines (below). Compatible with anionics, cationics, and nonionics, soluble in water in the presence of high concentrations of electrolytes, acids, and alkalies. When R′ contains a second carboxylic acid group, products show a very low order of skin and eye irritation.

Uses: Cosmetic and toilet preparations, fabric softener (which can be removed from substrate by increase in pH to the alkaline side).

N-*Alkylbetaines,* $RN^+(CH_3)_2CH_2COO^-$

These materials are zwitterionic at pHs at and above their isoelectric points (neutral and alkaline pHs) and cationic below their isoelectric points (acid pHs). They show no anionic properties. Compatible with all classes of surfactants at all pHs except that at low pHs they yield precipitates with anionics. Acid and neutral aqueous solutions are compatible with alkaline earth and other metallic ions (Al^{+++}, Cr^{+++}, Cu^{++}, Ni^{++}, Zn^{++}). They show minimum skin irritation at pH = 7. Show constant adsorption onto negatively charged surfaces (as cationics), irrespective of pH. Slightly better wetting and foaming properties at acidic than at alkaline pHs. Hard water has no effect on foaming properties in aqueous solution. Emulsification properties are similar to those of β-*N*-alkylaminopropionic acids (not good for paraffinic oils).

Uses: Similar to those of β-*N*-alkylaminopropionic acids.

2. pH-Insensitive Zwitterionics

These materials are zwitterionics at all pHs (at no pH do they act merely like anionics or cationics).

Sulfobetaines, Sultaines, $RN^+(CH_3)_2(CH_2)_xSO_3^-$

Adsorb onto charged surfaces at all pHs without forming hydrophobic films. Good lime soap dispersants.

Uses: Similar to other zwitterionics. Lime soap dispersants in soap-detergent formulations.

II. SOME USEFUL GENERALIZATIONS

Anionics are generally not compatible with cationics, and vice versa; nonionics and zwitterionics are compatible with all other types.

Carboxylic acid salts are more sensitive to low pH, polyvalent cations, and inert electrolyte in the aqueous phase than salts of organic phosphoric acids, and these in turn are more sensitive than organic sulfates or sulfonates.

Branched-chain or ring-containing surfactants are generally more soluble and show lower viscosity in aqueous media than straight-chain materials with the same number of carbon atoms; on the other hand, the latter are much more biodegradable than the former. Fluorocarbon chains, even when straight, are resistant to biodegradation.

Organic sulfates are readily hydrolyzed by hot acids; esters are readily hydrolyzed by hot alkali (or hot acids). Amides are more resistant to hydrolysis by hot acids or alkali than organic sulfates or esters, respectively.

Nonquaternary cationics are generally sensitive to high pH, polyvalent anions, and inert electrolyte in the aqueous phase; quaternary ammonium salts, on the other hand, are generally insensitive to these additives.

Oxyethylenation of any type of surfactant usually results in an increase in its solubility in water and a decrease in its sensitivity to pH change or electrolyte.

Oxyethylenation of hydrophobes that are acidic (carboxylic acids, phenols) or basic (amines) leaves essentially no nonoxyethylenated hydrophobe, whereas oxyethylenation of alcohols generally leaves an appreciable amount of unreacted hydrophobe.

Polyoxyethylenated fatty acids prepared by the reaction of fatty acids with polyoxyethylene glycols are a mixture of mono- and diesters, whereas those prepared by the reaction of fatty acids with ethylene oxide contain only monoesters.

Edible ester-type surfactants can be based on glycerol, sorbitol, or propylene glycol. The foam stabilization and viscosity-thickening

properties of diethanolamine—fatty acid condensates are related directly to their diethenolamide content; on the other hand, solubility in water is shown only by the 2:1 condensate.

Mercaptan-based nonionics are prone to develop a somewhat unpleasant odor and are unstable to oxidizing agents.

N-Alkylaminoacids are sensitive to pH change, developing the characteristics of cationics at low pHs and those of anionics at high pHs. Zwitterionics containing a quaternized *N* and one carboxylate group (alkyl betaines) show the characteristics of cationics at low pHs, but show no anionic characteristics at high pHs. Sulfobetaines are insensitive to pH change.